

POLYAMINE DERIVATIVES, A PROCESS TO MAKE THEM, AND THEIR USE

The invention relates to a process to make polyamine derivatives with at least one anchoring group and at least one matrix-compatible moiety, the polyamine derivatives so obtainable, and the use of such polyamine derivatives in conventional applications, such as pigment dispersants in inks, wetting agents in coating compositions, and transfer resins in pigment processing operations.

EP-A-0 358 358 discloses the use of specific amine derivatives as pigment dispersing agents. However, such conventional polyester based pigment dispersants (see also WO 98/19784) often lead to crystallisation problems, particularly when they are used in acryloyl-functional acrylic resin-based compositions. Further, some conventional pigment dispersants contain salt bridges, which is undesired.

There is a need for alternative pigment dispersing agents in the art, especially for applications such as printing inks, varnishes, and coating compositions that can be cured chemically and/or photochemically. These alternative agents preferably have better dispersing properties than the conventional pigment dispersants and preferably are suitable in virtually all conventional applications, without any further processing steps, such as the re-heating of the formulation to (re)dissolve any precipitate, being required. Finally, the alternative agents should preferably be substantially free of salt bridges.

Acryloyl-functional resin-based coating compositions have become more popular, since they are very useful in coating compositions which are cured by at least a UV curing step. There is a specific need for alternative pigment dispersing agents for UV cure applications, such as UV curable printing inks, varnishes, and coating compositions.

The present invention relates to alternative agents that are of use as pigment dispersant. In a preferred embodiment it relates to specific polyamine derivatives containing matrix-compatible moieties.

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Surprisingly, we have found a process to make polyamine derivatives which are very versatile and typically will outperform the products of EP-A-0 358 358 and WO 98/19784 in pigment dispersing operations, particularly since the anchoring moiety of the polyamine derivatives has improved interaction with pigments, while the matrix-compatible moiety can be tailored to ensure full compatibility of the derivatives and the matrix in which they are used, particularly in combination with acryloyl-functional resins. Accordingly, we claim the process to make these polyamine derivatives, intermediates of the process, the products obtainable, and their use.

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The process according to the invention is characterised in that one or more polyamines, each with one or more $-NH_2$ functions and one or more second amine functions, said second amine functions having a lower lactone reactivity than said $-NH_2$ functions, is reacted in a first step with one or more lactones, hydroxyacids, cyclic carbonates, or mixtures thereof, to form a polyamine-derived compound with amide and/or urethane groups, which polyamine-derived compound is reacted in a second step with one or more at least bifunctional amine-specific reagents to form an intermediate optionally comprising ester and/or carbonate groups, wherein in the second step optionally an additional amine modifier of formula III)

25 $(Y)_x(Y'')_y(Y')_zNH_{3-x-y-z}$ III)

wherein x is an integer of 0, 1 or 2, y is an integer of 0, 1 or 2, z is an integer of 0 or 1, wherein $x+y$ is 1 or 2, $x+y+z$ is 1 or 2, Y represents an (anchoring) moiety with affinity for a pigment surface or substrate, Y'' represents a (stabilising) moiety with affinity for the matrix, and Y' represents a further group that is neither an anchoring

moiety nor a stabilising moiety, is co-reacted, and in the intermediate at least two polyamine residues, or if a modifier is co-reacted, at least one polyamine residue and at least one optional amine modifier residue, are linked by said bifunctional amine-specific reagent.

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Affinity for the matrix as used herein means that a mixture of the matrix and the moiety with affinity for the matrix as such gives a homogeneous solution. In thermodynamic terms this means that the interaction between the matrix and the moiety with affinity for the matrix should be better than theta (for theta conditions see "Introduction to Polymers", 2nd edition, p. 162, by R.J. Young and P. A. Lovell).

10 Affinity of a compound for the pigment surface or the substrate as used herein is determined by dissolving the compound in the matrix in a known concentration. This solution is subsequently mixed with 5 wt% of pigment particles or substrate particles (the substrate particles having a size about 1 mm), respectively, at 15 atmospheric conditions. After 24 hours of mixing, the concentration of the compound in the matrix is determined again. If the concentration of the compound has decreased the compound has an affinity for the pigment or substrate, respectively.

20 In a preferred embodiment the process according to the invention is characterised in that one or more polyamines, each with one or more -NH₂ functions and one or more second amine functions, said second amine functions having a lower lactone reactivity than said -NH₂ functions and wherein each second amine function, independently, can be primary or secondary, is reacted in a first step with one or 25 more lactones, cyclic carbonates, hydroxyacids, or mixtures thereof, to form a polyamine-derived compound comprising unreacted second amine function, amide and/or urethane groups, optionally ester and/or carbonate groups, and one or more -OH groups, which compound is reacted in a second step with an at least bifunctional amine-specific reagent to form an intermediate comprising at least two

polyamine residues with amide and/or urethane groups and optionally ester and/or carbonate groups that are linked by said amine-specific reagent residue.

If so desired, any conventional catalyst may be used in either the first or the
5 second step. The molecular ratio in which the polyamines are reacted with said lactones, cyclic carbonates, hydroxyacids, or mixtures thereof can vary over a wide range. Preferably, on average at least 0.1, more preferably at least 0.5, most preferably at least 1 lactone, cyclic carbonate and/or hydroxyacid molecule is reacted per $-NH_2$ function in the reaction mixture of the first step. Similarly,
10 preferably on average at most 10, more preferably at most 5, even more preferably at most 3, still more preferably at most 2, and most preferably at most 1.5 lactone, cyclic carbonate and/or hydroxyacid molecule is reacted per $-NH_2$ function.

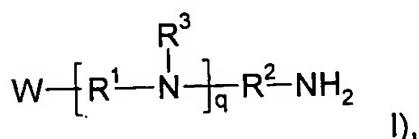
The linked polyamine residue(s) with amide and/or urethane groups and optional
15 ester and/or carbonate groups were found to form an "anchoring group" with very good interaction (affinity) with pigments and plastic surfaces. Depending on the molar ratio of the reactants in the first step and the nature of the at least bifunctional amine-specific reagent, it is possible to tailor the anchoring group to optimise this interaction. Optionally, but less preferred, the process comprises an
20 intermediate step wherein the $-OH$ groups, or parts of the unreacted amine groups, are reacted before the step wherein the polyamine residues are linked with the at least bifunctional amine-specific reagent. If this intermediate step is performed, then care is to be taken that the second amine functions survive the reaction step, in order to allow the linking to occur.

25 The polyamines used in accordance with the invention are substituted or unsubstituted, linear or branched, hydrocarbons containing one or more $-NH_2$ groups and one or more second amine functions with a lower lactone reactivity than said $-NH_2$ functions. Although less preferred, these polyamines may also

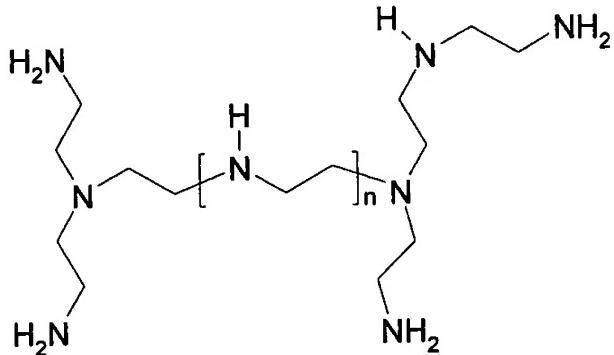
possess other less reactive groups, e.g. hydroxyl groups. Further, although also less preferred, the polyamines may only contain amine groups with a comparable reactivity which in a first step are reacted with less than 1 equivalent of the lactone, cyclic carbonate or hydroxyacid compound. To establish whether or not the amine groups of the polyamine have the necessary difference in reactivity towards lactones and/or cyclic carbonates, one can start from common general knowledge with respect to the reactivity of amines, including the knowledge that, in such reactions, primary amines are more reactive than secondary amines, and primary amines on secondary carbon atoms are more reactive than primary amine groups on tertiary carbon atoms. Helpful is the simple test wherein 1 mole of ε-caprolactone is reacted with a mixture comprising 1 mole of a low-molecular weight mono-amine analogue with said -NH₂ group and 1 mole of a low-molecular weight mono-amine analogue with said second amine function. The reaction can be performed with or without solvents at a temperature where reactivity is observed which can be monitored with, e.g., a titration on amines. Suitably the reaction is conducted at 100°C for a period of 16 hours. Low-molecular weight compounds are suitably compounds with a molecular weight of from 50 to 150 Dalton. In the test but, if this can be analysed, preferably in the reaction of the polyamine, at least 60%, on a molar basis, of the lactone, hydroxy acid and/or cyclic carbonate reacts with the more reactive -NH₂ functions. More preferably, at least 70%, on a molar basis, of the lactone, hydroxyacid and/or cyclic carbonate reacts with the -NH₂ function, and most preferably, at least 80%, on a molar basis, of the lactone, hydroxyacid and/or cyclic carbonate reacts with the more reactive -NH₂ functions.

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Preferred polyamines are compounds of formula I),



wherein q is an integer from 1 to 10, preferably 1 to 5, more preferably 1 or 2, R¹ and R², independently, represent alkylene groups with from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, each of R³ being independently selected from hydrogen, hydroxyalkyl, alkylamine, polyalkylamine, and polyalkylpolyamine, and
 5 W is hydroxy or amine. Preferably, R¹ and R² are the same. Examples of products according to formula I) include: diethylene triamine (q=1), triethylene tetramine (q=2), tetraethylene pentamine (q=3), triethylene tetramine (q=1, R³ is ethylamine), dipropylene triamine (q=1), dihexylene triamine (q=1), and compounds of the



general branched structure

prepared

10 from aziridine and known as polyethylene imine and commercially available under the tradename Epomin® SP with Mw's up to 10,000 or similar, e.g. compounds having propylene rather than ethylene moieties, or compounds with more or less primary, secondary, or tertiary amine groups. The compounds can also comprise a combination of ethylene, propylene and/or hexylene units.

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The lactone, hydroxyacid and/or cyclic carbonate can be selected from any conventional lactone, hydroxy acid and/or cyclic carbonate, including, but not limited to, butyrolactones, valerolactones, caprolactones, ethylene carbonate, propylene carbonate, glycerol carbonate, hydroxy stearic acids, hydroxybutyric acids, and hydroxycaproic acid. Preferably, a conventional lactone is selected. The lactones can be of the beta-, gamma-, delta- and/or epsilon-type. In view of their stability and availability, gamma-, delta-, and epsilon-lactones are most preferred.
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The product of the first step is reacted with an at least bifunctional amine-specific reagent. By amine-specific is meant that if the polyamine-derived compound comprises both the second amine function and -OH groups, then at least 60%, on a molar basis, of the amine-specific reagent groups will react with the second 5 amine function. Preferably, at least 80%, most preferably at least 90%, both on a molar basis, of the amine-specific reagent groups will react with the second amine function of the product of the first step. Preferably, the specificity of the reaction is measured by analysing the reaction product of the process according to the invention. However, if this is not feasible, then a simple test method can be used 10 wherein a mixture comprising an equal molar amount of a low-molecular weight mono-OH-functional analogue and a low-molecular weight analogue compound with just one second amine function is reacted in a suitable solvent at a temperature of 65°C, optionally in the presence of a solvent, until at least 80%, preferably at least 90% of the amine has reacted with the amine-specific reagent, 15 after which the specificity of the reaction can be determined using conventional techniques.

The amine-specific reagent is typically used in an amount wherein the number of amine-reactive groups corresponds to from 0.1 to 10 times the number of second 20 amine function groups of the product of the first step. In a preferred embodiment, the amine-specific reagent is used in an amount wherein the number (in equivalents) of amine-reactive groups corresponds to from 1 to 10 times the number (in equivalents) of second amine function groups of the polyamine-derived compound. In particular, if the amine-specific reagent comprises three or more 25 reactive groups, up to 10 times equivalent amine-reactive groups on 1 equivalent second amine function group will still provide sufficient crosslinking in the resulting intermediate of the reaction between the amine-specific reagent and the product of the first step. By sufficient crosslinking is meant that, on average, at least two amine-functional compounds are linked to an amine-specific reagent. Preferred

amine-specific reagents include isocyanates, anhydrides, acid chlorides, epoxy compounds, maleates, fumarates, citraconic esters, itaconic esters, and (meth)acrylates. More preferably, the amine-specific reagent is a conventional di- or poly-isocyanate, including compounds such as hexylene-1,6-diisocyanate, 5 isophorone diisocyanate, toluene diisocyanate, and oligomeric or polymeric diphenyl methane diisocyanate (MDI). It is to be understood that if the amine-specific reagent comprises more than two amine-reactive groups, then these additional groups may or may not have reacted with amine functions of the same or other polyamine-derived compound molecules.

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The intermediate from the second reaction step comprises -OH groups, which are reacted in a third step of a preferred process with compounds that introduce a "matrix-compatible moiety". By matrix-compatible is meant that said moiety has affinity for the continuous medium in which the final polyamine derivative is to be 15 used as dispersant, wetting agent, or the like. Preferably, the polyamine derivative is used in coating compositions and printing inks, most preferably in acryloyl-functional resin-containing compositions. Non-aqueous coating compositions and printing inks are preferred. The matrix-compatible moiety has a molecular weight of more than 250, preferably more than 500, more preferably more than 800, even 20 more preferably more than 1,200 and, most preferably, more than 2,000 Dalton, with the molecular weight preferably being below 20,000, more preferably below 10,000 Dalton. If the polyamine derivative is to be used in aqueous compositions, e.g. as a paint dispersant in water-borne coating compositions, then the third step 25 preferably comprises an alkoxylation process. Said alkoxylation process can comprise one or more ethoxylation and/or propoxylation steps, in any order or sequence.

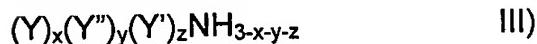
If the polyamine derivative is to be used in non-aqueous compositions, then at least part of the OH groups of the intermediate is preferably reacted with an

epoxide, lactone, cyclic carbonate, (hydroxy) acid, ester, anhydride, etc., to substitute a linear or branched, substituted or unsubstituted, preferably unsubstituted, C₄-C₃₀ alkyl, polyester, polyether, polyetherester and/or polyester-ether group for the proton.

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It should be noted that the polyamine derivative can be modified at any time during the process, provided that the final product resulting from the process bears at least one anchoring group and at least one matrix-compatible moiety. Two examples of preferred modifications are the following:

- 10 1.) in the second step of the process, at least one additional amine modifier is introduced of formula III),



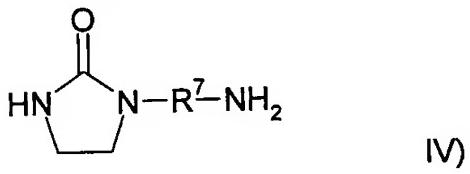
wherein x is an integer of 0, 1 or 2, y is an integer of 0, 1 or 2, z is an integer of 0 or 1, wherein x+y is 1 or 2, and x+y+z is 1 or 2, Y represents an (anchoring) moiety

- 15 with affinity for a pigment surface or substrate (such as a plastic article), Y'' represents a (stabilising) moiety with affinity for the matrix, and Y' represents a further group that is neither an anchoring moiety nor a stabilising moiety. Group Y' may be any group known by the person skilled in the art, but is preferably selected from the group of branched and unbranched alkyl and cycloalkyl groups, preferably

- 20 C₁-C₁₀ alkyl and cycloalkyl groups, more preferably C₃-C₁₀ alkyl and cycloalkyl groups. Preferably, group Y'' is selected from the group of linear or branched, substituted or unsubstituted, preferably unsubstituted, C₄-C₃₀ alkyl, polyester, polyether, polyetherester, and polyesterether. Preferably, group Y is an aliphatic group with from 2 to 10 carbon atoms containing at least one tertiary amino group

- 25 or a heterocyclic group containing at least one basic ring nitrogen atom and where the heterocyclic group may be attached to the NH group of formula III) by an alkylene group containing up to 10 carbon atoms. Preferred heterocyclic groups are optionally substituted triazole, pyrimidine, imidazole, pyridine, morpholine, pyrrolidine, piperazine, benzimidazole, benzthiazole and/or triazine. Substituents

may be C₁₋₆ and especially C₁₋₄-alkyl or alkoxy or amino. As noted hereinbefore, Y may be attached to the NH group via an alkylene group containing 2 to 10 carbon atoms, preferably it is a C₂₋₈-alkylene, more preferably a C₂₋₅-alkylene, and even more preferably a C₂₋₄-alkylene group. Y may also be attached to the NH group via a polyether group containing the same number of carbon atoms as the alkylene group. Examples of still more preferred products of formula III) are: nitrogen-substituted alkanediamines with an NH₂ group and a secondary or tertiary amine function, 1-(2-aminoethyl)-piperazine, 2-(1-pyrrolidyl)-ethylamine, 4-amino-2-methoxypyrimidine, products of formula IV),

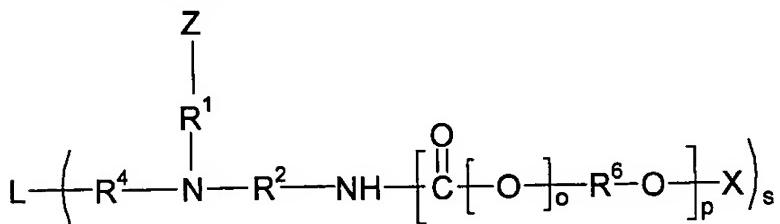


wherein R⁷ is an ethylene group, and Jeffamines®. Most preferably, the compounds are selected from the group consisting of N, N-dimethyl-1,3-propanediamine, 4-(2-aminoethyl)-pyridine, 2-amino-6-methoxybenzothiazole, 4-(aminomethyl)-pyridine, N,N-diallylmelamine, 3-amino-1,2,4-triazole, 1-(3-amino-propyl)-imidazole, 3-mercaptop-1,2,4-triazole, monofunctional Jeffamines®, and products of formula IV). The additional amine was found to be incorporated into the anchoring group, allowing further tailoring. The amount of at least bifunctional amine-specific reagent in the second step is to be adjusted such that sufficient bifunctional amine-specific reagent is present to also react with the additional amine.

2.) At least one (additional) monofunctional amine-specific reagent of formula V-A is present in the second step of the process, wherein V is selected from the group consisting of linear or branched, substituted or unsubstituted, preferably unsubstituted, C₄-C₃₀ alkyl, polyester, polyether, polyetherester, and polyester-ether, and A is an amine-specific reactive group as defined for the second step of the process. The additional monofunctional amine-specific reagent was found to

be attached to the anchoring group, allowing further tailoring of the final polyamine derivative, to optimise it for use in various media, using varying pigments and/or plastic substrates. The amount of at least bifunctional amine-specific reagent in the second step may be adjusted such that the total amount of reactive groups of 5 the at least bifunctional amine-specific reagent and the monofunctional amine-specific reagent is within the range of 1 to 10 times the number of second amine function groups of the reaction mixture.

In another preferred embodiment, the invention also relates to compounds 10 obtainable by the above-identified process which comprise said anchoring and matrix-compatible moieties. Such compounds can be represented by formula II):



II)

wherein each $R^4NR^1ZR^2NH$ moiety is a residue of the polyamine used, each 15 $C(O)[O]R^6O$ moiety is a residue of the lactone, hydroxyacid and/or cyclic carbonate used, and L is the residue of the at least bifunctional amine-specific reagent. R^1 and R^2 are as defined above for formula I. Depending whether or not a lactone, hydroxy acid or cyclic carbonate is used, each o will independently be 0, 0, and 1, respectively. The index p presents the average number of moiety $C(O)[O]R^6O$ per 20 $R^4NR^1ZR^2NH$ moiety and has a value ranging from 0.1 to 30, preferably from 0.1 to 10, more preferably 0.5 to 5, most preferably 1 to 3. The tail thus formed of 25 moieties $C(O)[O]R^6O$ preferably is of a non-crystallising nature and further, preferably, is not completely formed of caprolactone derivatives. For the molecules derived from the above-mentioned process, each X preferably is hydrogen. However, if the optional intermediate modification step as presented above is

taken or if the -OH group is reacted in later steps, then X is, wholly or partly, a substituted or unsubstituted, linear or branched, hydrocarbon group. The index s represents the number of products of the first reaction step that react with the amine-specific reagent and is an integer of 1 to 10. If s is 1, the amine-specific
5 reagent L is further reacted with a compound of formula III). Preferably, s is 1 to 4, most preferably s is 1 or 2. R⁴ presents group R³ minus a proton. R³ is as defined above for formula I). Z- presents a group W'-[R¹-NR⁵]_{q-1}-, wherein W' is W as defined for formula I above or the reaction product of group W with lactone, hydroxyacid and/or cyclic carbonate, and each R⁵ independently is a group R³ or
10 the reaction product of R³ with amine-specific reagent L.

The moiety of formula II), minus the groups X, was found to be a very suitable anchoring group for interaction with (affinity for) a variety of pigments and substrates. However, in order to make a good dispersant, the moiety is to be
15 combined with at least one matrix-compatible moiety to form suitable dispersants, wetting agents, compatibilisers, and the like. Accordingly, each group X, independently, preferably is such a matrix-compatible moiety. Typically, this is achieved by reacting the product of formula II), wherein X is hydrogen with a suitable compound. Preferably, each of the groups X, independently, is a
20 compound with a molecular weight of more than 250, preferably more than 500, more preferably more than 800, even more preferably more than 1,200 and, most preferably, more than 2,000 Dalton, and a molecular weight of preferably below 20,000, more preferably below 10,000 Dalton. In a preferred embodiment, the groups X are fully compatible with binder resins and/or the solvent of the
25 composition in which the products according to the invention are used.

In a further preferred embodiment the groups X are selected such that the final compound is fully compatible with acryloyl-functional resins. By fully compatible is meant that the groups X as such are fully soluble in the matrix. Preferably, the

groups X are, independently, selected from linear or branched, substituted or unsubstituted, preferably unsubstituted, C₄-C₃₀ alkyl, polyester, polyether, polyetherester or polyesterether groups. Preferably, the groups X are formed by reacting a compound of formula II), wherein X is hydrogen with appropriate 5 epoxides, lactones, cyclic carbonates, hydroxy acids, and other suitable conventional reactants to form polyesters, e.g. via an alternating co-polymerisation, and/or polyethers. Alternatively, a linear or branched, substituted or unsubstituted, preferably unsubstituted, C₄-C₃₀ alkyl, polyester, polyether, polyetherester or polyesterether with OH reactive groups is reacted with compound 10 II), with X is hydrogen. If so desired, conventional catalysts may be used in this step.

If the solvent of the composition in which the polyamine derivative is used is an organic solvent, it is most preferred that X comprises a polyester tail. If the solvent 15 of the composition in which the polyamine derivative is used is an aqueous solvent, it is most preferred that X comprises a polyether tail.

Especially good polyamine derivatives are obtained when the -OH function of the polar moiety is reacted in an alternating co-polymerisation with hexahydrophthalic 20 anhydride and Cardura® E10, to form a polyester function. Notwithstanding the above, if the compound of formula II as defined above comprises other moieties that are compatible with the solvent and/or binder resin of the composition wherein the compound of formula II is used, (part of) X may simply be a hydrogen atom. In this respect, further especially preferred polyamine derivatives are polyamine 25 derivatives comprising one or more groups derived from reaction with an amine modifier of formula III) described above, wherein this group acts as a stabilising group in the composition in which the polyamine derivative is used. Compounds of formula III) that can provide a group that acts as a stabilising group in water

include mono-functional Jeffamines®. Also, group Z of formula II) may act as a stabilising group in the composition in which the polyamine derivative is used.

The invention also relates to the use of the polyamine derivatives prepared by the
5 process given above in coating compositions or printing ink formulations. Preferably, the polyamine derivatives are used in a coating composition or printing ink formulation that comprises acryloyl-functional resins. The polyamine derivatives are of particular use as pigment dispersants in pigmented coatings and/or printing inks. In a more preferred embodiment the polyamine derivatives are used in a
10 coating or ink composition that is curable by actinic light irradiation, such as UV or IR irradiation. Most preferably, such compositions comprise acryloyl-functional resins. Other preferred uses of the polyamine derivatives are as a wetting agent or as adhesion promotion agent in a coating composition or as a transfer resin in pigment processing operations.

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The invention is elucidated by the following examples.

Example 1: Preparation of a pigment dispersant with polyester tails

a) Preparation of a hydroxy amide-amine:

20 Into a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N₂inlet, and a reflux condenser, 61.85 grams (0.60 mole) of diethylene triamine (ex Aldrich) and 136.85 grams (1.20 moles) of ε-caprolactone (ex Aldrich) were weighed. The reaction mixture was heated on an oil bath, at 140°C, for 10 h to complete the reaction. A polyamine-derived compound was obtained.

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b) Preparation of a tetrahydroxy-tetraamide-diurethane

Into a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N₂-inlet, and a reflux condenser, 96.90 grams (0.292 mole) of the polyamine-derived compound of Example 1a was weighed. The temperature was

raised to 65°C and 24.50 grams (0.146 mole) of hexamethylene diisocyanate (ex Fluka) were added over a period of 45 minutes while keeping the reaction mixture at 65°C. The temperature was next raised to 100°C in order to complete the reaction of forming a tetrahydroxy-tetraamide-diurea.

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c) Preparation of a pigment dispersant with polyester tails

Into a 500 ml three-necked round-bottomed flask equipped with a reflux condenser, a mechanical stirrer, and a thermometer 40.21 grams (48.4 mmoles) of the tetrahydroxy-tetraamide-diurea of Example 1b were weighed together with 10 132.75 grams (0.861 mole) of hexahydrophthalic anhydride (ex Lonza) and 0.39 grams of a chromium based catalyst (Accelerator AMC-2, ex Flevo Chemie). The reaction mixture was heated to 155°C. Next 215.26 grams (0.878 mole) of Cardura® E10 (ex Resolution) were added over a period of 2.5 hours. An additional hour completed the reaction.

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Example 2: Preparation of a pigment dispersant with imidazolidinone groups

a) Preparation of a hydroxy-amide-amine

Into a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N₂-inlet, and a reflux condenser, 106.54 grams (1.033 moles) of 20 diethylene triamine (ex Aldrich) and 20 grams of cyclohexane were weighed. The temperature was raised to 100°C (reflux) and next a mixture of 235.76 grams (2.065 moles) of ε-caprolactone (ex Aldrich) and 107.28 grams of t-amyl alcohol were added over a period of 2.5 hours. An extra two hours completed the reaction.

25 **b) Preparation of a tetrahydroxy-tetraamide-diurea block with additional imidazolidinone groups**

Into a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N₂-inlet, and a reflux condenser, 98.62 grams of the solution of the polyamine-derived compound of Example 2a were weighed together with 4.16

grams of K-Flex® XM-3323 (Ex King Industries), an amine-functional imidazolidinone. The temperature was raised to 80°C and next 26.3 grams (0.156 mole) of hexamethylene diisocyanate (ex Fluka) were added over a period of 30 minutes while keeping the reaction mixture at 80°C. The reaction was stopped 20 minutes after all isocyanate had been added.

c) Preparation of a pigment dispersant with polyester tails

Into a 250 ml three-necked round-bottomed flask equipped with a reflux condenser, a mechanical stirrer, a N₂-inlet, and a thermometer 20.05 grams (theoretical: 68.7 mmoles of hydroxy groups) of the resin solution of Example 2b were weighed together with 53.05 grams (0.344 mole) of hexahydrophthalic anhydride (ex Lonza) and 0.17 grams of a Zn-based catalyst (Nuodex® ZN12 ex Sasol). The reaction mixture was heated to 145°C. Next, 77.04 grams (0.318 mole) of Cardura® E10 (ex Resolution) were added over a period of 2.5 hours. An additional hour at 150°C completed the reaction.

Example 3: Preparation of a pigment dispersant with polyether tails

Into a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N₂-inlet, and a reflux condenser, 9.82 grams of the resin of Example 2a, 20 50 grams of t-amyl alcohol, and 93.00 grams of Jeffamine® M1000 (ex Huntsman) were weighed. The reaction temperature was raised to 60°C and 10.40 grams (61.8 mmoles) of hexamethylene diisocyanate were added over a period of 30 minutes. After 15 minutes the temperature was raised to 80°C and vacuum was applied in order to remove solvents.

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The product of the Examples showed very good pigment dispersant properties, had a desirable low viscosity, higher gloss, and was fully compatible with an acrylated resin, therefore no precipitate was formed, allowing the use of the formulation "as is", meaning that it does not require re-heating before use. It was

found to be an improvement over conventional products, also because the polyamine derivative was easily dissolved in the resin, while it allowed for a much easier dispersion of the pigment into the formulation.